Study of Preferential Solvation in Mixed Binary Solvent as a Function of Solvent Composition and Temperature by UV−Vis Spectroscopic Method

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Preferential solvation of *N*-ethyl-4-cyanopyridinium iodide and 2,6-diphenyl-4(2,4,6-triphenyl-1-pyridino)-phenolate [Reichardt's $E_T(30)$ dye] has been studied in ethanol + tetrahydrofuran, ethanol + acetonitrile and acetonitrile + tetrahydrofuran binary mixtures as a function of temperature and composition of mixed binary solvents. It has been found that besides solute−solvent interaction, solvent−solvent interaction plays an important role in determining the solvation characteristics.

Introduction

Solvation of a solute in a mixed binary solvent is a subject of current interest.[1] Experimental evidence suggests that the solute may induce a change in the solvent composition in the solvation sphere compared to that in the bulk.[2,3,4] The phenomenon is termed as "preferential solvation" (PS) and its origin is believed to be due to a difference in solute−solvent and solvent−solvent interaction. Electronic spectroscopy provides a suitable method for studying the phenomenon. It has been observed that the maximum energy (E) of charge-transfer transition in various solutes acts as reporter of local composition[5,6,7] and reflects the solute−solvent and solvent−solvent interaction at the microscopic level, embodying both nonspecific and specific modes of solvation. Usually, three parameters, namely, solvent polarity-polarizability, H-bond donation (HBD) ability or solvent acidity, and H-bond acceptance (HBA) ability or solvent basicity have been characterized to represent the various modes of solute−solvent interaction. These parameters are represented, respectively, by the solvatochromic parameters π^*, α and β[8] or SPP, SA and SB[1], describe the different modes of solvation interaction in pure solvent. An experimentally determined parameter in pure solvent can be fitted to a multiple linear correlation equation involving these empirical parameters. Recently,[1] it has been found that the parameters SPP, SA, and SB may also be utilized for characterizing solvent mixtures. They provide a good description for the "iso-solvation point," where the solvent molecules in the mixtures are assumed to contribute equally to the solvation sphere. Several theoretical studies have been made to interpret PS in terms of solute−solvent and solvent−solvent interactions.[9−12] Although all the theoretical models point to temperature dependence of PS, studies in this respect are very scanty. Our preliminary studies[13] on the effect of temperature on the PS characteristics of *N*-ethyl-4-cyanopyridinium iodide and 2,6-diphenyl-4(2,4,6-triphenyl-1-pyridino)phenolate [Reichardt's $E_T(30)$ dye][5] in an ethanol + acetone mixture, indicate that solvent nonideality plays a significant role in modifying PS. But studies on a variety of solvent mixtures are needed to get a detailed picture so that generalization is possible. To this end, we have studied the PS characteristics of *N*-ethyl-4-cyanopyridinium iodide and Reichardt's $E_T(30)$ dye in three mixed-binary solvents. It is known that the maximum transition energy for these compounds depends on the solvent polarity and acidity (HBD ability) and is rather insensitive to the basicity of the media.[5,14−16] We have chosen solvent mixtures where the cosolvents differ with respect to acidity and/or polarity. Thus ethanol (ETOH) + acetonitrile (ACN), ETOH + tetrahydrofuran (THF), and ACN + THF binary mixtures have been used to study PS characteristics at various temperatures (298 K−313 K). Results have been analyzed in terms of existing models of preferential solvation.

Experimental Section

N-ethyl-4-cyanopyridinium iodide was prepared by the method described in the literature.[17] A sample of the $E_T(30)$ dye was obtained as a generous gift from Professor Ch. Reichardt. The solvents were dried by standard procedure.[18] Commercial "dry ethanol" was refluxed for several hours with calcium oxide and then distilled. Traces of moisture and other oxidizable impurities in the solvents were eliminated by distillation with calcium hydride immediately prior to the experiment. Mixed solvents were prepared by adding the component solvents by volume. Care was taken to avoid contamination by moisture during mixing. Absorption spectroscopic measurements were taken on a SHIMADZU UV 2101 PC spectrophotometer. The temperature was controlled to within ±0.5 K by circulating water from a thermostat SHIMADZU TB-85. To ensure that thermal equilibrium had been established, data were recorded only when the absorption at a particular wavelength attained a steady value. To check the reproducibility, the band maximum value was taken for several replicate measurements. The values were within ±1 nm. The concentration of the solute varied from 10^{-3} to 10^{-4} (M) depending on the solvent composition.

Results and Discussions

Position of the CT band maximum shifts to the red with an increase in percentage of the relatively less-polar component in the binary mixture. Increase in temperature also brings about a red shift. The CT band in solution for both the solutes appear as broad and structureless, rendering the position of the band maximum somewhat inaccurate (within ±1 nm). However, the overall band shift is greater than this inaccuracy. Solvatothermocromism of the band is continuous and reversible, the bandwidth and shape do not change in the temperature range

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TABLE 1: Values of Maximum Transition Energy (E_{12}), $E_{12}^{(ideal)}$, PS Index (δ_{S1}) and K_{PS} in Different Solvent Mixtures at 298 K

	ethanol (1) + acetonitrile (2)				ethanol (1) + tetrahydrofuran (2)				acetonitrile (1) + tetrahydrofuran (2)			
x_1	E_{12}[a]	$E_{12}^{(ideal)}$ [a]	δ_{S1}	K_{PS}	E_{12} [a]	$E_{12}^{(ideal)}$ [a]	δ_{S1}	K_{PS}	E_{12} [a]	$E_{12}^{(ideal)}$ [a]	δ_{S1}	K_{PS}
					Reichardt's $E_T(30)$ dye [b]							
0.0	46.0	46.0	----	----	37.6	37.6	0.00	----	37.6	37.6	0.00	----
0.1	49.8	46.6	----	----	42.7	39.1	0.21	4.73	39.3	38.4	0.10	2.28
0.2	51.8	47.3	----	----	45.8	40.6	0.33	4.97	40.6	39.3	0.16	2.22
0.3	52.9	47.9	----	----	47.9	42.0	0.38	5.34	41.7	40.1	0.18	2.22
0.4	53.4	48.6	----	----	49.2	43.5	0.38	5.44	42.4	41.0	0.18	2.00
0.5	53.5	49.2	----	----	50.0	45.0	0.33	5.17	43.0	41.8	0.15	1.80
0.6	53.2	49.8	----	----	50.4	46.5	0.26	4.27	43.5	42.6	0.11	1.57
0.7	52.9	50.5	----	----	50.6	47.9	0.18	3.10	44.0	43.5	0.07	1.37
0.8	52.5	51.1	----	----	50.9	49.4	0.10	2.22	44.5	44.3	0.03	1.15
0.9	52.3	51.8	----	----	51.4	50.9	0.03	1.53	45.2	45.2	0.00	1.06
1.0	52.4	52.4	----	----	52.4	52.4	0.00	----	46.0	46.0	0.00	----
					N-ethyl-4-cyanopyridinium iodide[c]							
0.0	67.8	67.8	0.00	----	55.0	55.0	0.00	----	55.0	55.0	0.00	----
0.1	70.9	68.7	0.25	4.89	60.5	57.2	0.13	3.07	57.1	56.3	0.08	1.77
0.2	72.9	69.6	0.39	5.51	64.2	59.3	0.20	2.97	58.9	57.6	0.13	1.75
0.3	74.2	70.4	0.43	6.22	66.9	61.5	0.23	2.86	60.4	58.8	0.15	1.70
0.4	74.8	71.3	0.40	5.83	68.8	63.6	0.22	2.65	61.7	60.1	0.15	1.65
0.5	75.1	72.2	0.33	4.87	70.2	65.8	0.19	2.38	62.7	61.4	0.14	1.51
0.6	75.1	73.1	0.23	3.24	71.3	68.0	0.14	2.05	63.6	62.7	0.11	1.37
0.7	75.0	74.0	0.13	1.93	72.3	70.1	0.08	1.72	64.5	64.0	0.08	1.23
0.8	75.2	74.8	0.04	1.32	73.4	72.3	0.04	1.44	65.3	65.2	0.05	1.03
0.9	75.6	75.7	0.00	0.87	74.8	74.4	0.01	1.22	66.2	66.5	0.02	0.78
1.0	76.6	76.6	0.00	----	76.6	76.6	0.00	----	67.8	67.8	0.00	----

[a] kcal mol^{-1}. [b] Uncertainty in E_{12} and $E_{12}^{(ideal)}$ ±0.1, uncertainty in K_{PS} ±0.2, uncertainty in δ_{S1} ±0.02. [c] Uncertainty in E_{12} and $E_{12}^{(ideal)}$ ±0.3, uncertainty in K_{PS} ±0.4, uncertainty in δ_{S1} ±0.03.

TABLE 2: Values of dE_{12}/dT as a Function of Solvent Composition in Various Solvent Mixtures

	dE_{12}/dT[a]				
	Reichardt's $E_T(30)$ dye			*N*-ethyl-4-cyanopyridinium iodide	
x_1	ethanol (1) + acetonitrile (2)	Ethanol (1) + tetrahydrofuran (2)	acetonitrile (1) + tetrahydrofuran (2)	ethanol (1) + acetonitrile (2)	acetonitrile (1) + tetrahydrofuran (2)
0.0	−0.02	−0.02	−0.02	−0.04	−0.03
0.1	−0.03	−0.03	−0.02	−0.07	−0.02
0.2	−0.04	−0.04	−0.02	−0.08	−0.02
0.3	−0.04	−0.04	−0.02	−0.08	−0.02
0.4	−0.05	−0.05	−0.02	−0.07	−0.02
0.5	−0.05	−0.04	−0.02	−0.05	−0.02
0.6	−0.05	−0.04	−0.02	−0.04	−0.03
0.7	−0.05	−0.04	−0.02	−0.03	−0.03
0.8	−0.04	−0.04	−0.02	−0.03	−0.04
0.9	−0.04	−0.03	−0.02	−0.04	−0.04
1.0	−0.03	−0.03	−0.02	−0.06	−0.04

[a] kcal mol^{-1} K^{-1}.

studied and no isosbestic point is observed in the spectrum. All these facts indicate that the shift of band maximum is not caused by change of equilibria between different chemical species in solution. The observed band-shifts were independent of the concentration of the solute in the range of concentration studied indicating the absence of solute−solute interaction.

Values of maximum transition energy, E_{12}, expressed in kcal mol^{-1} for different systems at various compositions at 298 K are listed in the Table 1. For a fixed composition, E_{12} is a linear function of temperature (T), but the value of dE_{12}/dT depends on the solvent composition (Table 2). For an "ideal" solvation behavior, the observed value of transition energy in a binary solvent mixture, E_{12}, would be given by the mole fraction average value of the transition energies in pure component solvents.[2] Thus

$$E_{12}^{(ideal)} = x_1E_1 + x_2E_2 \tag{1}$$

In the above equation x represents mole fraction and subscripts 1 and 2 represent the component solvents. The values of $E_{12}^{(ideal)}$ are also listed in the Table 1. Note that the observed values of E_{12} differs from $E_{12}^{(ideal)}$ values significantly for ETOH + ACN and ETOH + THF mixtures. For the ACN + THF mixture the deviation of the observed value from the ideal value is relatively small. Deviation of an observed solute property from the ideal value is often described in terms of preferential solvation of the solute.[2,3,6,7,19,20] The positive value of the deviation indicates that the solute is solvated preferentially by the solvent component having a higher E value. Thus, both the solutes are preferentially solvated by ethanol over acetonitrile or tetrahydrofuran over the entire composition range. It is known that ethanol interacts with the molecules of the solutes specifically through hydrogen bonding interaction.[5−7,11] Thus the preference of ethanol over ACN (or THF) can be rationalized in terms of a difference in the specific interaction (through hydrogen bonding) of the solute molecule with the component solvents. Small differences of acidity and polarity-polarizability of the solvents lead to a small extent of PS in the case of the ACN + THF mixture.

It was shown earlier that if we neglect solvent−solvent interaction during a spectroscopic transition, the observed E_{12} values are given by,[6,21]

$$E_{12} = x_1^L E_1 + x_2^L E_2;\ x_1^L + x_2^L = 1 \qquad (2)$$

where x_i^L represent the local mole fraction of the ith solvent component.

The extent of PS is often represented by the dimensionless quantity

$$\delta_1 = [E_{12} - E_{12}^{(ideal)}]/(E_1 - E_2) = (E_{12} - x_1E_1 - x_2E_2)/(E_1 - E_2) \qquad (3)$$

We have from eqs 2 and 3

$$\delta_1 = x_1^L - x_1 \qquad (4)$$

Thus the dimensionless parameter, δ_1, represents the excess or deficit of the component 1 in the local region with respect to the bulk. The values are also given in the Table 1. In our calculation, we have chosen the more polar of the two component solvents as the component 1. Another parameter, suitable for describing the temperature variation of PS characteristics is given as follows.

$$K_{PS} = (x_1^L x_2)/(x_2^L x_1) \qquad (5)$$

The value of K_{PS} may be obtained from the experimentally determined parameters as,

$$K_{PS} = [(E_{12} - E_2)/(E_1 - E_2)](x_2/x_1) \qquad (6)$$

The parameter K_{PS} is related to the equilibrium[11]

$$\bar{2} + 1 == \bar{1} + 2 \qquad (7)$$

where $\bar{1}$ and $\bar{2}$ represent component solvent molecules in the local (cybotactic) region, while *1* and *2* represent those in the bulk. In this context, note that for Reichardt's $E_T(30)$ dye in ethanol + acetonitrile, the value of E_{12} attains a maximum value in an intermediate solvent composition ($x_{ETOH} \approx 0.5$). Similar behavior has also been observed for this system by other workers.[22] Maximum or minimum of several properties for aqueous−organic binary mixtures also finds support from molecular dynamics simulation studies, where strong water-cosolvent interaction has been indicated.[23−25] Appearance of an extremum in an intermediate composition cannot be explained in terms of eq 2, where E_{12} is written as a weighted average. As stated earlier, eq 2 is valid when solvent−solvent interaction is small, but it may not be valid in the event of existence of strong solvent−solvent interaction. In the present case, the results may be explained in terms of strong ETOH-ACN interaction, presumably due to formation of 1:1 hydrogen bond between the solvent components. The values of dE_{12}/dT for this solvent mixture also show a maximum at 1:1 molar ratio of solvents. Thus, determination of local mole fraction for this solvent mixture using $E_T(30)$ dye is not possible. The values of δ_1 and K_{PS} calculated for other cases have been listed in the Table 1.

Expression for K_{PS} can be obtained by using the existing models of PS.[9−11] For 'pseudo-ideal' solvent behavior, i.e., in absence of solvent−solvent interaction, all the models indicate that K_{PS} would be independent of solvent composition at a constant temperature.[13] Variation of *ln* K_{PS} at constant temperature as a function of x_1 is shown in the Figure 1. The values of *ln* K_{PS} are indeed dependent on the solvent composition, indicating that solvent nonideality plays a role in determining the PS characteristics. We now discuss the effect of solvent nonideality on PS in the light of different models. According to the *two-phase model of solvation*,[11] where the solvent molecules are assumed to be distributed between the local and the bulk phase at equilibrium, the value of K_{PS} is determined by solute−solvent and solvent−solvent interaction and can be expressed as

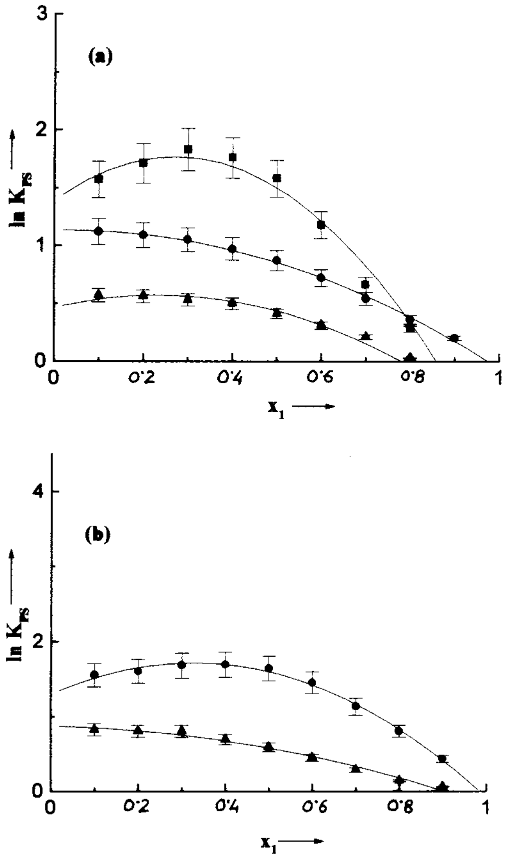

Figure 1. Plot of ln K_{PS} vs x_1 (mole fraction of more polar component) in mixed binary solvents. (a) *N*-ethyl-4-cyanopyridinium iodide in ethanol + acetonitrile (■), ethanol + tetrahydrofuran (●) and acetonitrile + tetrahydrofuran (▲) (b) Reichardt's $E_T(30)$ dye in ethanol + tetrahydrofuran (●) and acetonitrile + tetrahydrofuran (▲).

$$kT\ lnK_{PS} = [\epsilon_{S2} - \epsilon_{S1}] + [(N_1 - N_2)\epsilon_{12} - (N_1^0 - N_2^0)\epsilon_{12}^0 - N_1\epsilon_{11} + N_1^0\epsilon_{11}^0 + N_2\epsilon_{22} - N_2^0\epsilon_{22}^0 + (\epsilon_{11} - \epsilon_{22})/2 - (\epsilon_{11}^0 - \epsilon_{22}^0)/2] \qquad (8)$$

here ϵ_{Si} and ϵ_{ij} are energies of solute-i-solvent and i-solvent-j-solvent interactions, N_i is the number of i-solvent molecules, and the superscript 0 indicates the bulk phase. Terms in the first square bracket in the right-hand side of eq 8 are the contribution of solute−solvent interaction, while the terms in the second square bracket are due to solvent nonideality effect. When $\epsilon_{11} = \epsilon_{22} = \epsilon_{12}$ and $\epsilon_{ij} = \epsilon_{ij}^0$, the term in the second square bracket becomes zero. Only under this condition (pseudo-ideality), will the value of *ln* K_{PS} be independent of the solvent composition. To get an idea about the variation of *ln* K_{PS} with solvent composition, we proceeded as follows. The eq 8, with the assumption $\epsilon_{ij} = \epsilon_{ij}^0$, meaning that interactions between solvent components in the local region are the same as that in

TABLE 3: Values of Δ*H* (kJ mol^{-1}) as a Function of Solvent Composition

	Reichardt's E$_T$(30) dye		*N*-ethyl-4-cyano pyridinium iodide	
x$_1$	ethanol (1) + tetrahydrofuran (2)	acetonitrile (1) + tetrahydrofuran (2)	ethanol (1) + acetonitrile (2)	acetonitrile (1) + tetrahydrofuran (2)
0.1	−2.5 ± 0.4	−1.2 ± 0.2	−9.2 ± 1.4	3.6 ± 0.5
0.2	−3.4 ± 0.5	−0.3 ± 0.02	−10.8 ± 1.6	3.4 ± 0.5
0.3	−4.3 ± 0.6	0.0 ± 0.02	−11.3 ± 1.7	3.4 ± 0.5
0.4	−7.2 ± 1.1	1.6 ± 0.2	−7.4 ± 1.1	3.1 ± 0.5
0.5	−4.8 ± 0.7	3.1 ± 0.5	2.7 ± 0.4	2.2 ± 0.3
0.6	−3.7 ± 0.6	0.8 ± 0.1	11.9 ± 1.8	1.7 ± 0.3
0.7	0.0 ± 0.02	6.4 ± 1.0	20.7 ± 3.1	0.0 ± 0.02
0.8	1.5 ± 0.2	7.3 ± 1.1	25.7 ± 3.9	−1.6 ± 0.2
0.9	2.3 ± 0.3	8.2 ± 1.2	27.6 ± 4.1	−3.3 ± 0.5

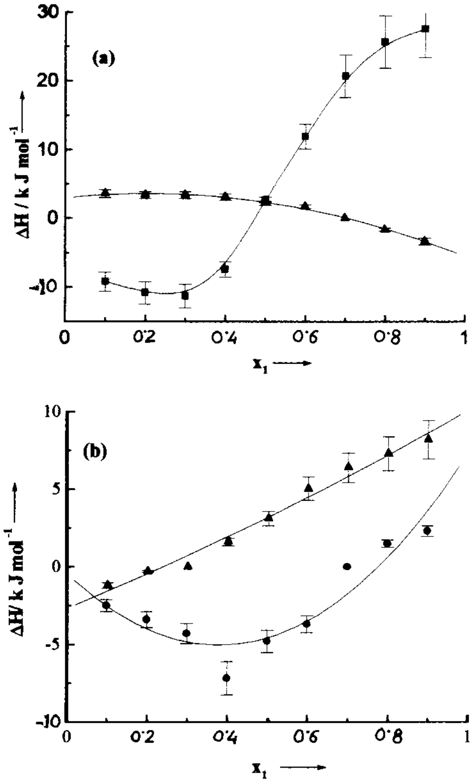

Figure 2. Plot of Δ*H* vs x$_1$ (mole fraction of more polar component) in mixed binary solvents. (a) *N*-ethyl-4-cyanopyridinium iodide in ethanol + acetonitrile (■) and acetonitrile + tetrahydrofuran (▲) (b) Reichardt's E$_T$(30) dye in ethanol + tetrahydrofuran (●) and acetonitrile + tetrahydrofuran (▲).

the bulk, gives

$$kT \ln K_{PS} = (\epsilon_{S2} - \epsilon_{S1}) + 2(N_1 + N_2)\Delta\epsilon_{12}[(x_1^{L} - x_1) + x_1(1 - (N_1 + N_1^{0} + N_2 + N_2^{0})/2(N_1 + N_2))] + constant \quad (9)$$

where $\Delta\epsilon_{12} = 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$.

According to eq 9 for a fixed solvent composition, a plot of $\ln K_{PS}$ versus $1/T$ would thus be linear, provided that the coordination number of the solute, N_1+N_2, is independent of temperature. A linear plot, as found in the present case, indicates that in the small temperature range, N_1+N_2 may be taken as approximately constant. This approximation, however, is not valid for a wider temperature range.[26] The values of Δ*H* for the equilibrium (eq 7) obtained from the slope of $\ln K_{PS}$ versus $1/T$ plot for various system are given in the Table 3. Δ*H* values depend on solvent composition, as may be seen from the Figure 2. Δ*H* represents the heat change associated with replacement of one molecule of 2 in the local phase by one molecule of 1 in the bulk. As such, due to the existence of solvent−solvent interaction, the value is expected to depend on the bulk composition. The negative/positive value of Δ*H* indicates that heat is liberated/absorbed in the process. From the eq 9 we get

$$-\Delta H/N_A = (\epsilon_{S2} - \epsilon_{S1}) + 2(N_1 + N_2)\Delta\epsilon_{12}[(x_1^{L} - x_1) + x_1(1 - (N_1 + N_1^{0} + N_2 + N_2^{0})/2(N_1 + N_2))] \quad (10)$$

where $\Delta\epsilon_{12} = 2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}$ and N_A is the Avogadro number.

In our experiment, solvent component 1 is the more polar component [e.g. in the *E$_T$(30)* scale] and thus it interacts with the solute to a greater extent. Considering that ϵ_{Si} values are negative quantities, we have ($\epsilon_{S2}-\epsilon_{S1}$) as a positive quantity. In the present case, the first term in the square bracket in eq 10 is positive ($x_1^{L} > x_1$), but the second term is negative and largely compensates the positive term (N_1+N_1^{0}+N_2+$N_2^{0} \gg N_1$+N_2). Thus a negative value of $\Delta\epsilon_{12}$ would make Δ*H* negative. A positive value of $\Delta\epsilon_{12}$, on the other hand, would make Δ*H* positive or slightly negative, depending on the relative magnitudes of solute−solvent and solvent−solvent interaction. The following general observation may now be made from the Δ*H* values (obtained within the limit of experimental inaccuracy of ca. 15%). For ACN + THF mixture using both the solutes, the value of Δ*H* is positive or slightly negative. This can be explained by assuming a positive sign of $\Delta\epsilon_{12}$, which indicates that interaction between like-solvent molecules is relatively greater than that between unlike-solvent molecules. Thus, the present results indicate that the component solvent molecules repel each other in ACN + THF mixture. There is, however, a difference in solvation behavior for the two solutes at the acetonitrile end. For the E$_T$(30) dye, the value of Δ*H* is approximately zero within experimental uncertainty, where the mole fraction of ACN ranges from 0.0 to 0.4. Beyond this region, Δ*H* shows an increasing trend as the mole fraction of the ACN increases. Thus, when the mole fraction of ACN is high, the effect of solvent−solvent interaction predominates. This is consistent with the self-aggregation of ACN molecules in this region. Probing the solvent−solvent interaction using *N*-ethyl-4-cyano pyridinium iodide as the indicator solute also points to a positive value of $\Delta\epsilon_{12}$. But a decreasing trend is observed, however, as the percentage of ACN in the mixture increases. The ETOH + THF mixture studies, using the E$_T$(30) dye, indicate a negative value of Δ*H* particularly around x$_1$ ~0.5. This is also true for the ETOH + ACN mixture for *N*-ethyl-4-cyanopyridinium iodide in the composition range $0 < x_1 < 0.5$. The results indicate that in this mole fraction range the solvent components attract each other. This may rationalized in view of attractive interaction between ETOH and the cosolvent (ACN/THF), possibly through hydrogen bonding. In the alcohol-rich region the self-associated structure of ETOH predominates, making $\Delta\epsilon_{12}$ positive. A positive value for Δ*H* results.

Conclusion

Electronic spectroscopic study using suitable-indicator solutes may be used to investigate PS characteristics in a binary solvent mixture as a function of temperature and solvent composition. The extent of PS depends primarily on the difference of specific solute-solvent interaction. Besides a difference in the interaction of the solute molecules with the molecules of the component solvents, PS characteristics are modified by solvent−solvent interaction in a mixed binary solvent.

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